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液相溶胶包裹修饰法制备煤制天然气甲烷化催化剂的研究

Study on the Coal to Substitute Natural Gas Methanation Catalysts Prepared by Liquid Sol Coated Modification Method

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摘 要

鉴于当今的能源现状、全世界对环境保护的诉求以及我国的能源储量结构，合理高效地使用煤炭资源越来越凸显重要性。煤炭利用技术已经在以合成氨为主要代表的行业大量应用，相关技术日渐成熟，尤其是煤制代用天然气。但是，煤制天然气过程的关键技术之一是合成气制甲烷，其中尚存在若干问题需要解决。例如，镍基催化剂作为主流的甲烷化催化剂其抗硫性差、高温下易烧结和积碳失活、活性组分与载体作用太强等缺点还有待弥补。

为了寻求性能更佳的甲烷化催化剂，本论文基于固定床管式反应器对制备的一系列催化剂进行活性评价，并运用一系列表征手段对催化剂进行测试，最终确定了最佳的复合载体 $MgO\text{-}Al_2O_3$ 以及最佳复合载体中 MgO 的含量。此外，考察了焙烧温度、金属助剂 La 和活性组分 Co 的添加对催化剂活性的影响。

本文研究获得的主要结果如下。

（1）采用液相溶胶包裹修饰法制备了系列 $NiO/MO_X\text{-}Al_2O_3$(M=Si，Zr，Mg)催化剂。反应前在 $10\%H_2/N_2$ 气氛下 400^oC 还原 3h。考察不同复合载体对催化剂活性的影响。结果表明，加入 Si、Zr 和 Mg 后，活性组分 Ni 与载体 Al_2O_3 之间的相互作用得以减弱，利于催化剂在低温下的还原。系列 $NiO/MO_X\text{-}Al_2O_3$ 催化剂的活性明显依赖于载体中添加的第二金属氧化物的种类。不同载体所制镍基催化剂中 CO 转化率依次为： $NiO/MgO\text{-}Al_2O_3$> $NiO/ZrO_2\text{-}Al_2O_3$> $NiO/SiO_2\text{-}Al_2O_3$> NiO/Al_2O_3。

（2）在催化剂 $NiO/MgO\text{-}Al_2O_3$ 中，使 MgO 含量在 0%-20%（以催化剂为基准的重量百分比，下同）之间变化，以考察 MgO 添加量对催化活性的影响。研究结果表明，当 MgO 含量为 10%时，对催化剂活性的促进作用最大，在各反应温度下均表现出比其他 MgO 含量的催化剂更高的活性。同时发现，高 MgO 添加量（20%）的催化剂较之低 MgO 添加量（5%）的催化剂更适合在高温下反应。利用 X 射线衍射(XRD)、氮气吸附脱附(BET)、程序升温还原(TPR)、二氧化碳程序升温脱附(CO_2-TPD)等表征方法对催化剂进行研究，结果可见，由于 MgO 的晶格大小与 NiO 相近，可以在晶胞中与 NiO 互换，与 NiO 形成固溶体，其结果是 MgO 替代了一部分 NiO 与载体 Al_2O_3 紧密结合，使得催化剂表面的游离镍

增多，从而促进氢在催化剂表面的吸附。而表面吸附的氢越多，在催化剂表面由CO分解生成的活性碳物种以及氧物种能够加速转化为CH_4和CO_2，促进催化剂吸附的CO从催化剂表面脱除释放，从而为CO的再吸附提供新的活性位点，加速了CO的吸附。在这个过程中，CO转化反应速率提升，即催化剂的活性得到提高。

（3)将上述所制高活性10%NiO/10%MgO-Al_2O_3催化剂分别在400^oC、500^oC和600^oC温度下焙烧，结果表明焙烧温度对催化剂活性有显著影响。提高焙烧温度使得活性组分Ni与载体Al_2O_3之间的相互作用增强，导致活性组分镍更难于在低温下还原，最终造成催化剂甲烷化活性大幅度降低。

（4）通过单因素考量La_2O_3含量不同对催化剂活性有影响后，结合MgO添加量和焙烧温度，采用正交试验方法，综合考察了以上三个因素对催化剂活性的影响。结果显示，在本文所选择的因素水平条件下，以焙烧温度对催化剂活性的影响为最大。在所设定的条件下，5%La_2O_3-5%MgO-400^oC的催化剂甲烷化性能最佳。助剂La_2O_3在催化剂中主要是通过促进NiO在载体Al_2O_3表面的分散，以及减弱NiO与载体之间的相互作用而起作用。

（5）添加Co作为甲烷化催化剂的第二活性组分Co，结合还原温度与焙烧温度，综合分析了各因素对催化剂活性影响的大小。经过方差分析得到：对于给定的显著性水平α，焙烧温度和钴镍配比对催化剂活性有高度显著的影响，还原温度对催化剂活性有显著的影响，还原温度和焙烧温度的交互作用对催化剂活性有影响。固定Ni含量的条件下，在本文试验条件范围内，Co添加量越大，催化剂活性越高。

关键词：

镍基催化剂；CO甲烷化；液相溶胶包裹修饰法；复合载体；表面碳；活性组分；游离镍

Abstract

In the light of the situation of the energy supply, universal environmental protection appeal and the energy resource structure of our country, how to use the coal resources efficiently has been more and more important. The technologies for coal utilization technology have been applied greatly in many fields, represented by synthetic ammonia industry. Its relevant technology has matured, especially for coal synthesis gas. The crucial step to this technology is the technology from syngas to methane, which still leaves some questions need to be solved. For example, as current main catalyst, Ni-based catalysts' sulfur resistance are bad, and conventional nickel catalysts easily suffer from severe deactivation resulting from sintering of Ni particles and coke disposition during the exothermic methanation reaction. Also, the interaction between the active component and the support is too strong. All these defects are needed to be overcome.

In order to obtain more efficient catalysts for methanation, based on fixed bed reactor, the best composite support MgO-Al_2O_3 and the optical contents of MgO has confirmed via testing and characterizing the series catalysts in this dissertation. The effects of calcined temperature, La content and Co content on the performance of supported catalysts are also studied.

The predominant results obtained are generalized as follows:

(1) By using liquid sol coated modification method, series of NiO/MO_X-Al_2O_3 (M=Si，Zr，Mg) catalysts were prepared. Before the reaction, all catalysts were reduced in 10%H_2/N_2 atmosphere for 3h to explore the effect of composite oxide supports on the catalytic performance of Ni-based catalysts. It was found that the interaction between the active component Ni and the support Al_2O_3 were weakened after incorporating Si, Zr, Mg, which was beneficial for catalyst reducing at low temperature. The catalytic performance of the NiO/MO_X-Al_2O_3 catalyst was found to be different, depending on the identity of second metal oxides (MOx) added. The activity trend of different NiO/MO_X-Al_2O_3 catalysts followed: NiO/MgO-Al_2O_3>NiO/ZrO_2-Al_2O_3> NiO/SiO_2-Al_2O_3>NiO/Al_2O_3.

(2) According to the investigation of the effect of MgO contents, from 0% to 20%(mass ratio), in NiO/MgO-Al_2O_3 on the catalytic performance, we discovered that methanation activity reached the highest, assuming the better activity than other catalysts with the different MgO loadings at every reaction temperature when MgO loadings got 10%. Also, 20% MgO loading catalyst trended to perform catalytic reaction at high temperature than 5% MgO loading catalyst. The catalysts were characterized by XRD, BET, TPR and CO_2-TPD. The results obtained indicate that: MgO crystal lattice is similar to NiO lattice in size, thus it can be interchangeable with NiO, forming solid solution with it, whose results are MgO substituting for a part of NiO to combination with Al_2O_3 tightly. All these makes the free nickel on catalyst surface increasing and promotes hydrogen adsorption on the catalyst surface. When the hydrogen in the ambience is enough, surface carbon and oxygen species formed through CO dissociation would speedily convert to CH_4 and CO_2 and desquamate from the surface to provide adsorption center for CO re-adsorbed and consequently accelerate CO adsorption. As a result, CO conversion rate speeds up and the catalyst performance improves.

(3) The high activity 10%NiO/10%MgO-Al_2O_3 catalyst prepared above were calcinated at 400°C, 500°C and 600°C, the result implied that different calcination temperature makes great difference to catalyst activity. The interaction between the active component Ni and the support Al_2O_3 is strengthened during calcination process, whose result is that the reduction of NiO becomes hard, bringing about the methanation activity decreasing greatly.

(4) After searching into the effect of La_2O_3 loadings on catalyst by single factor analysis method, integrating with MgO loadings and calcination temperature, we synthetically explored these three factors' effects on catalysts adopting orthogonal experiment. The results showed that calcination temperature makes the greatest influence on catalytic performance under the factor levels we selected. The